

Chain Transfer to a Surface—a Novel Method for Forming Polymer Nanofilms

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Motivation—One of the hallmarks of nanomaterials is their high surface area. Controlling surface properties are therefore critical to their synthesis, processing, and often their usefulness. Polymers have long been a popular coating for modifying surface properties of a wide range of materials. The surface properties of a polymer are generally dictated by the top few nanometers, but it is difficult to synthesize pinhole-free nanoscopic polymer films. The ability to grow, through an *in-situ* polymerization, ultrathin polymer films opens a wide range of surface functionalizations for nanoparticles and nanomaterials. Applications include solubilization and compatibilization of nanomaterials, and synthesis of active polymer films with extremely fast kinetics.

Accomplishment—We have developed a method of functionalization a wide range of surfaces, with an equally wide range of polymers. Any surface that can support a self-assembled monolayer can be functionalized by any polymer capable of undergoing a radical polymerization.

The basic synthetic scheme is shown in Fig. 1, using a silicon oxide surface with a silane coupling agent as an example. A monolayer coating of a chain transfer agent is applied to the substrate and a solution of monomer and free radical initiator covers the surface. The radical initiator is initiated, and a fraction of the initiators that are near the surface when they become free radicals are able to transfer their free radical to the surface. The surface bound radical is then able to initiate the growth of a surface bound polymer. This polymer grows for a very short time before undergoing a chain

termination event, whether chain transfer, recombination, or some side reaction. The kinetics of the steps in this polymerization are critical to the resultant polymer film.

Figure 2 shows a plot of film thickness for the synthesis of two polymers, poly(N-isopropyl acrylamide) (pNIPAM) and poly(methyl methacrylate) (PMMA), using this method. The film thicknesses in the pNIPAM system reveals an interesting behavior based upon the system's kinetics. The linear increase at low monomer concentrations is due to the expected linear increase in polymer molecular weight. At higher concentrations, the viscosity of the solution becomes an issue. This viscosity increase slows the diffusion of free radicals to the surface, lowering the graft density. The net effect of the reaction kinetics is that the reaction is self-limiting. Film synthesized by this method is necessarily nanoscopic, and are generally pinhole-free.

Significance—A simple and versatile method to form continuous ultrathin polymer films using only commercially available reagents has been developed. This synthetic technique has a multitude of applications to microfluidics, biotechnology, nanomaterials preparation and functionalization, etc. Traditional techniques for forming *in-situ* polymer films have required laborious synthesis of custom initiators, and carefully controlled reaction conditions (concentrations, purities, inert atmospheres, etc.). This method requires none of these. Using this technique, a minimally skilled lab worker can prepare a wide range of high quality surface bound polymer films on most of the commonly encountered surfaces and particles.

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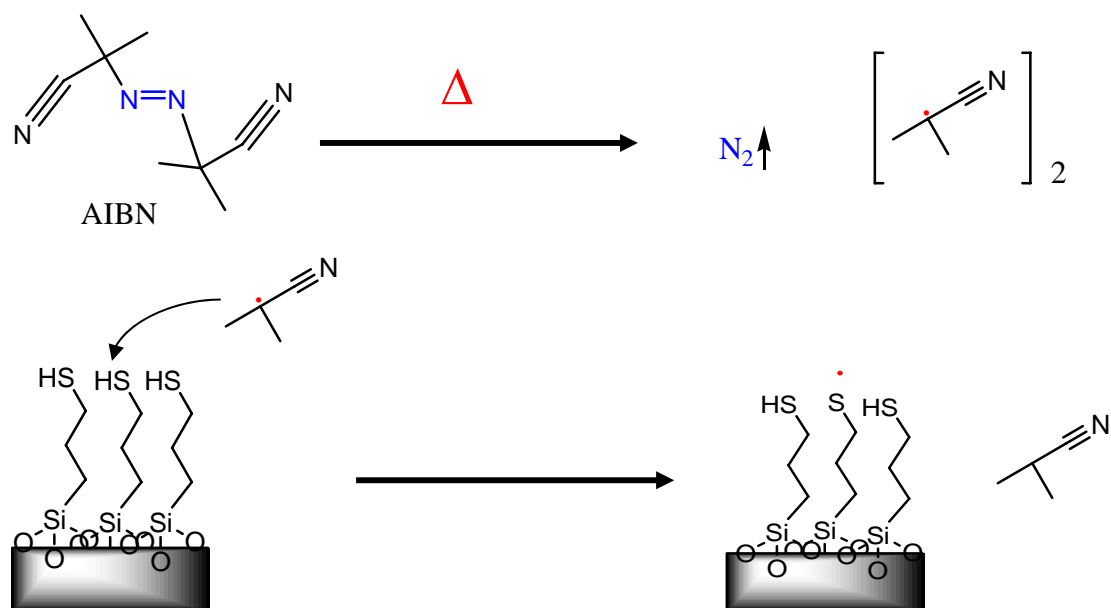


Figure 1. Reaction scheme for a chain transfer to a surface. Free radicals are generated in solution, and transferred to the surface via proton abstraction. The surface bound radical is then capable of initiating a surface bound polymer.

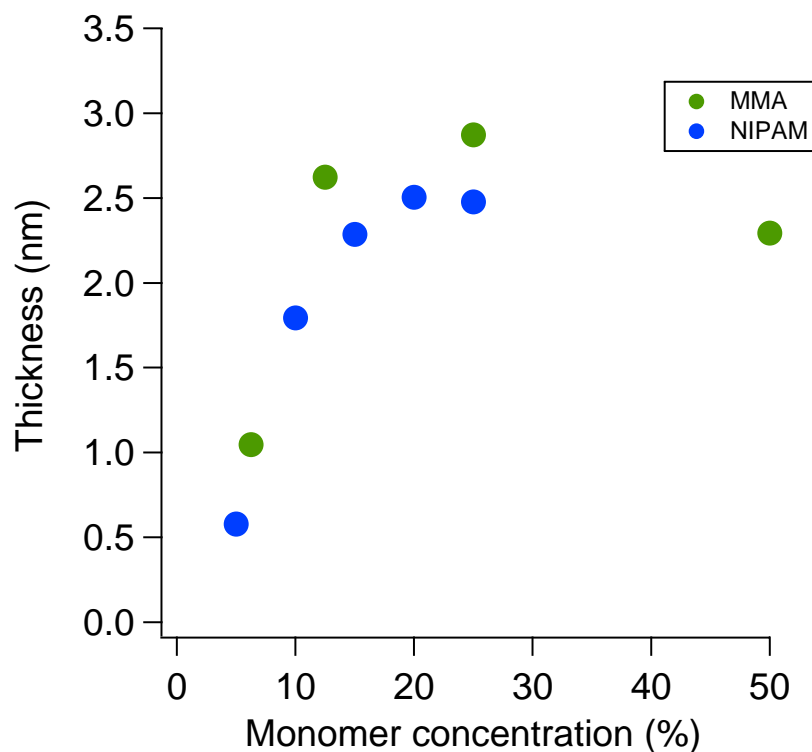


Figure 2. Thickness of polymer films as a function of the monomer concentration, with all other reaction conditions held constant. At low monomer concentration the thickness increases due to increasing molecular weight, while at high monomer concentration the thickness decreases due to decreasing graft density.